2011 Ballard Bio-Reactor Pilot Test Results Spring - Fall 2011

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Introduction

This mine water treatment summary report was prepared to evaluate the performance of the selenium-reducing biological pilot treatment system installed and operated at the historic Monsanto Ballard Mine site northeast of Soda Springs, Idaho. The implementation of this treatment study supports the requirements of the Administrative Settlement Agreement and Order on Consent/Consent Order for Remedial Investigation/Feasibility Study (2009 CO/AOC). The 2009 CO/AOC is a voluntary agreement between P4, the United States Environmental Protection Agency (USEPA), the Idaho Department of Environmental Quality (IDEQ), the United States Department of Agriculture, Forest Service (USFS), the U.S. Department of the Interior (DOI), Bureau of Land Management (BLM), and the Shoshone-Bannock Tribes. The 2009 CO/AOC is being implemented under the USEPA's Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) authority.

A fixed-bed, up-flow anaerobic biological treatment system was selected for full scale field testing following a comprehensive survey of available selenium control technologies based on a variety of project parameters and selection criteria, including: (i) the ability to meet Idaho surface water quality standards, (ii) complexity, (iii) previously demonstrated, (iv) low quantities of waste generated, (v) cost, and (vi) flexibility for treating varying concentrations of multiple metallic species. This decision was supported by the small scale treatability test conducted at the Horseshoe Overburden area (HOA) at the South Rasmussen Mine between June and September 2008 which consistently demonstrated efficient removal of Se and other metals (AMEC, 2008)

The primary objectives of this study are to operate a Se treatment system on the seepage stream emanating from an overburden stockpile located within the inactive Ballard Mine site to reduce the release of Se from this area while simultaneously providing information to determine the compatibility of this remediation technology to meet Idaho surface water quality standards (IDSWQS) within the phosphate mining area (IDAPA, 2011).

Background

Approximately 20 million cubic yards of overburden rock were removed from the Ballard Mine pits between 1952 and 1969, which allowed the removal of 11 million tons of phosphate ore to be trucked to the mining company's elemental phosphorus plant near Soda Springs. The majority of the overburden material was stockpiled in 317 acres of waste rock dumps and the remaining backfilled into the pits. Many of these waste dumps were partially reclaimed, including experimental plantings by the USFS out of Logan, Utah. Today, the Ballard pits remain largely open (partially backfilled or not backfilled) and waste rock dump material predominately exposed and uncovered (Lee, 2000). A surface stream emanating from the toe of waste rock stockpile, MWD082, flows away from the toe towards the north and was found to contain Se concentrations measured at 380 μ g/L (ppb) and levels of Cd, Zn, and Ni above IDSWQS. Pertinent IDSWQS data is presented in **Table 1**. The stream flow begins during the spring runoff period with a duration of three to five months depending on annual precipitation levels.

Table 1. Idaho Surface Water Quality Standards. All metal limits are for dissolved concentrations except Selenium.

Parameter	As	Cd ^(a)	Cr ^{III(a)}	Cr ^{VI}	Cu ^(a)	Pb ^(a)	Ni ^(a)	Se	Zn ^(a)		DO
	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	pН	(ppm)
IDSWQS ^(b)	150	1.3	230	11	37	15	170	5	380	6.5 - 9	>6

(a) The Idaho Surface Water Quality Standards (IDSWQS) for these metals are hardness dependent and were calculated using the equations in Section 210 from the *Rules of the Department of Environmental Quaitiy,IDAPA 58.01.02 "Water Quality Standards".* Referred to hereafter as the IDAPA 58.01.02. It should also be noted that paragraph 210.03.c.i of the IDAPA 58.01.02 states, "The maximum hardness allowed for use in those equations shall not be greater than four hundred (400) mg/l, as calcium carbonate. As the average hardness concentration in the water samples was 1940 mg/l the maximum allowed value of 400 mg/l was used to calculate the IDSWQS.

The Aquatic life Chronic Criteria (CCC) from Section 201.01 of the IDAPA 58.01.02 were used for the IDSWQSs.

System Design, Construction, and Startup

Maximum water flows at the MWD082 site were estimated to be approximately 30 gpm during spring run-off with a low of less than 1 gpm after August. A retention pond equipped with a HDPE liner was constructed near the base of the waste rock pile to collect the seepage for storage prior to passage through the bioreactor system. The retention pond and bioreactor system were enclosed in a fenced area. For a schematic process flow diagram of the process the reader is referred to the *Ballard Mine MWD082 Seepage Pilot Treatability Study: Test Work Plan and Sampling and Analysis Plan* (MWH, 2010).

Three separate treatment trains were constructed with pre-cast concrete tanks (14' X 8'deep X 6 wide') and loaded with a layer of 4" inert gravel to distribute influent flows, 12 X 20 Nirit Darco granular activated carbon (GAC growth media), and 3/8" to 3/4" crushed limestone. Reactor 1 contained a 50/50 GAC to limestone mixture, and reactors 2 & 3 contained a 40/60 mixture of limestone to GAC. Each system contained approximately 10% freeboard or void volume after installation of treatment media to provide 10 gpm rate per train at a 3 hour residence time. Two 110V solar pumps were used to supply water from the pond to the reactor trains. Power was supplied to each pump via 12-185 Watt solar panels connected to a series of 10-12V rechargeable batteries. Each battery train was configured for 120V nominal output. **Figures 1** and **2** contain images of the bioreactor systems immediately following construction.

Figure 1. The Three Bioreactors, Sand Filter, and Retention Pond.





Figure 2. The Solar Panels for the Bioreactor System at Southeast Ballard Mine.

Reactor influent was dosed with 1 to 2 gallons per hour (gph) carbon nutrient consisting of MicroCg[™] as a source of dissolved respirable organic carbon diluted in pond water. The target total organic carbon (TOC) influent concentration was 10 ppm to minimize the reduction of sulfate and the formation of biofilm and carbonate precipitates that could plug the system. **Figure 3** shows the carbon dose tank inside the conex box. The system influent was then split and delivered to the base of each reactor and allowed to flow up through the gravel and reactive

media layers prior to discharging to a common header that delivered the combined reactor effluent to a sand filter to remove suspended particulate matter. Effluent from the sand filter was then discharged to the seepage or re-circulated to the pond to maintain water levels for the test.

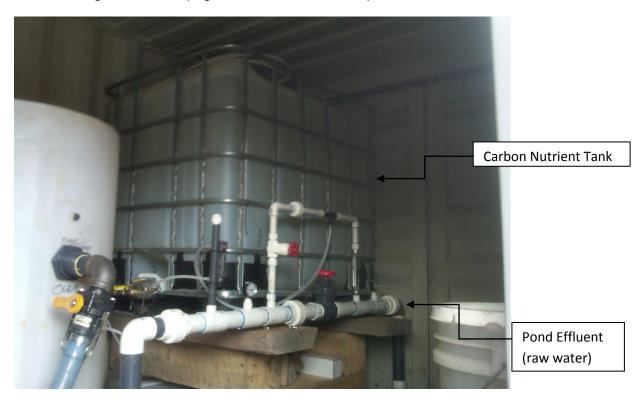


Figure 3. Carbon Nutrient Tank Mixing with Pond Effluent.

On May 12, 2011, each reactor was inoculated by dumping 15 gallons of fine-grained sediment on top of each reactor's media bed and washed down into the media with water from the adjacent pond. The sediment was collected from the nearby drainage. It was assumed this sediment had the propensity to contain an active microbial population capable of reducing soluble selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) to immobile elemental selenium. Each reactor was then filled with water from the pond and 5 gallons of methanol and 2 gallons of molasses was added and washed into the reactor as well.

Every three days the tanks were re-circulated by turning over approximately three pore volumes over a six hour period, after which the power was disconnected to begin a three day static growth period. The recirculation and static growth cycle continued until Se levels were below 5 ppb on May 26th then continuous flow through process began.

Samples were acquired as outlined in the *Ballard Mine MWD082 Seepage Pilot Treatability Study Test Work plan and Sampling and Analysis Plan*, section 6.0. Samples were acquired throughout the test from the pond effluent (PE), reactor 1 effluent (R1), reactor 2 effluent (R2), reactor 3 effluent (R3), combined reactor effluent (CBE), and sand filter effluent (SF) streams. Samples were measured in the field for dissolved oxygen (DO), oxidation-reduction-potential (ORP), temperature, conductivity, pH, and total dissolved solids (TDS).

All samples were submitted to Microbac laboratories for analysis for arsenic (total and dissolved), biological oxygen demand (BOD), cadmium, chloride, copper, fluoride, iron, magnesium, manganese, nickel, nitrate, ammonia, total phosphorus, potassium, selenium (total and dissolved), sodium, sulfate, total dissolved solids, total suspended solids, TOC, vanadium, zinc, calcium. Filtered samples were passed through a 45 µm pore size filter media. All field and lab data is available in **Appendix 1**.

Pilot Test Operations Results

Pond effluent had an average pH of 7.4. The initial pond effluent pH of approximately 8 decreased throughout the operating season due to the recirculation of sand filter effluent with a decreased pH of approximately 6.8 due to microbial activity. These pH trends are portrayed in **Figure 4**. It is notable that the average pond effluent pH is comparable to that observed in the recirculation pond during the 2008 field study, however, the bioreactor and sand filter effluents have a slightly higher pH than effluent water during the 2008 study due to the neutralizing ability of basic limestone growth in each reactor. It is recommended that pH adjustment from limestone be continued during future operation to maintain IDSWQS pH between 6.5 and 9.

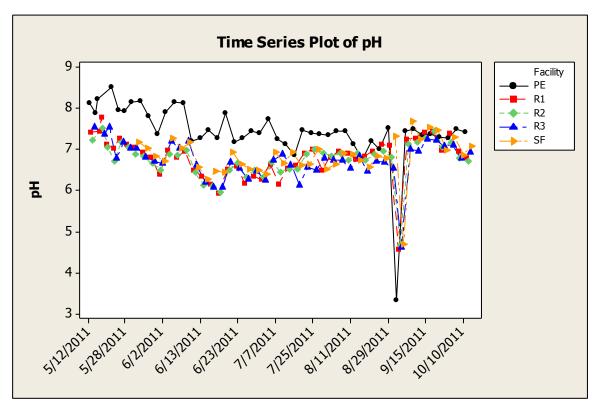


Figure 4. Time Series plot of pH.

DO and ORP measurements taken in the field are key indicators for the Se reducing ability of the system. Initially the pond effluent was oxidizing with a DO concentration of 13.36 ppm and an ORP of +216 mV. After the two week static growth period, bioreactor and sand filter effluent

DO concentrations decreased significantly indicating that microbial respiration removed DO and established reducing conditions as shown in **Figure 5** and **Figure 6**. Similar to the pH trend, DO and ORP levels in the pond effluent material decreased slightly during the test due to intermittent recirculation to the pond. It is notable that bioreactor and sand effluent contained less than 6 ppm DO required by IDSWQS to support aquatic life. Although it is likely that the DO increases above 6 ppm a few moments after discharge, a simple re-oxygenation process will be required for system effluent prior to discharge to the natural outfall.

The original project premise was to treat water containing approximately 400 ppb Se, however, the bioreactor treatment systems offer flexibility to remove Se at various levels. Over the course of the test the Se concentration in the retention pond decreased 85% from a high of 2410 ppb in May to a low of 354 ppb on October 13th when the last samples were obtained prior to system shutdown as shown in **Figure 7**. The marked decrease in Se content in the pond was partially due to intermittent recirculation from the sand filter discharge to maintain a pond water level high enough to support process flow rates. History has shown the initial run-off period during the spring contain the highest metals values being flushed out of waste rock piles. The system had to be operated by alternating from discharge to the original drainage and recirculation to the pond on a semi-weekly basis in order to maintain enough water to treat at desired flow rates. There was no Se speciation data acquired during the course of the test to determine selenate and selenite species distribution, however, previous data suggests selenate was the predominate form and the bioreactor system does not preferentially reduce one form over the other.

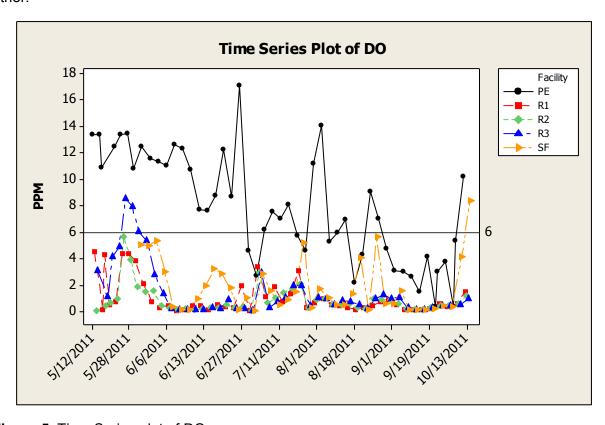


Figure 5. Time Series plot of DO.

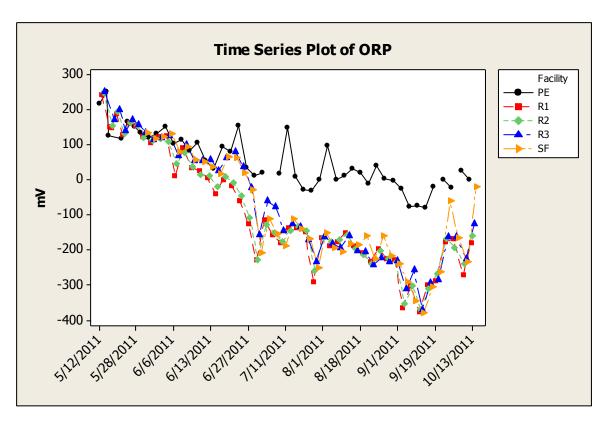


Figure 6. Time Series plot of ORP.

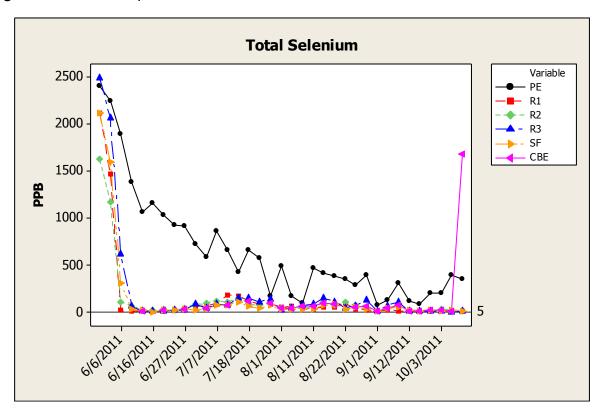


Figure 7. Time Series Plot of Total Se.

Idaho surface water quality standards for Se are on a total basis, however, monitoring dissolved Se provides insight on the microbial activity since particulate containing Se can be removed via physical filtration in the reactor growth media and sand filter. Total Se concentrations were slightly higher than dissolved Se for all samples, indicating a lack of filtration of Se containing particulate above 45 µm. For example, total and dissolved Se content in the sand filter effluent is displayed in **Figure 8**, where it is observed that particulate Se is approximately twice as high as dissolved Se. The inefficiency of the sand filter to remove particulate Se implies that modifications are required to improve sand filter operations. The sand filter was raked to clear the system of accumulated particulate. It is notable that the sand filter and bioreactor trains were not equipped with backwash or fluidization capabilities to remove suspended solids, and neither of these more complex technologies was required to maintain flow through the system.

Shortly after system inoculation, recirculation, and start-up period the dissolved Se content decreased from 2,330 ppb to below the 5 ppb target for all three reactor trains throughout June. In early July Se levels increased slightly above 5 ppb where they remained through the remainder of the operating season. This trend is portrayed in **Figure 9**. During this period total and dissolved Se removal efficiency decreased from >99% to <90% as depicted in **Figure 10**. The Se removal data presented in figures 7 through 10 indicate that the removal of significant quantities of Se from high Se influent levels can be achieved easily whereas the removal of smaller quantities of Se from influent with lower Se are more difficult to achieve. This suggests that the system operations must be tuned (i.e., increased residence time, higher carbon feed rate, etc.) to reduce Se under these conditions, or a polishing step must be added to the effluent of this system to meet the 5 ppb target.

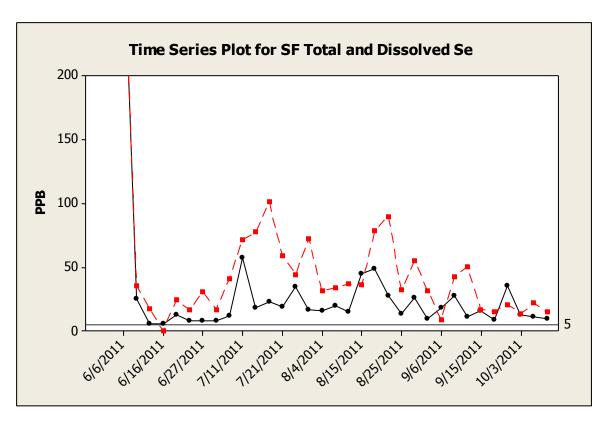


Figure 8. Time Series Plot for Dissolved (black) and Total (red) Se Content in the Sand Filter Effluent.

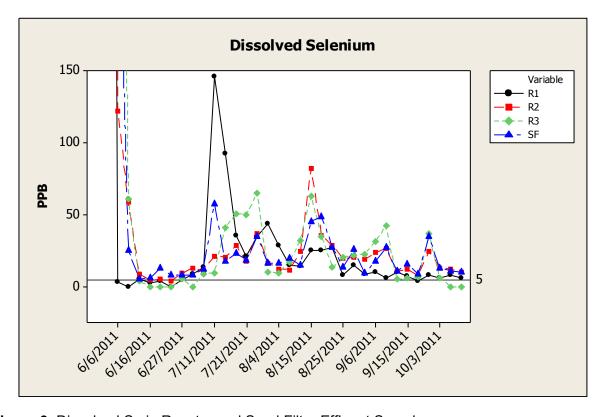


Figure 9. Dissolved Se in Reactor and Sand Filter Effluent Samples.

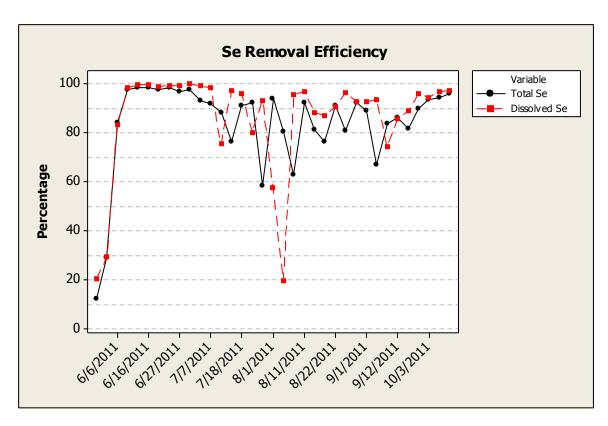


Figure 10. Instantaneous Total and Dissolved Se Removal Efficiency between Pond and Sand Filter Effluent Streams.

A variety of operating variables were altered in an attempt to reduce Se below 5 ppb, including: decreasing system flow rates, adding ammonia and phosphate macronutrients from liquid ammonium phosphate (10-34-0 fertilizer), switching carbon nutrient sources (microbial food) from MicrocG® to a methanol/molasses mixture, changing the level of carbon nutrient addition. However, none of these modifications were able to consistently reduce Se to below the 5 ppb target, likely due to the sluggish biological response time. **Figure 11** and **Figure 12** display ammonia and total phosphorus content, respectively, above the native pond effluent from macronutrient addition. It should be noted that seepage from this phosphate mining waste pile did not leach significant amounts of bio-available phosphate to support microbial growth, thus the decision to add the liquid fertilizer, 10-34-0. On two occasions the system was shut-down to fix pump problems and in the mean time was dosed with carbon nutrient for a three day static growth period in an attempt to improve microbial activity. Following the static growth period Se removal was below 5 ppb due to the long retention time, however, when returned to normal flow through the effluent Se levels returned to >5 ppb.

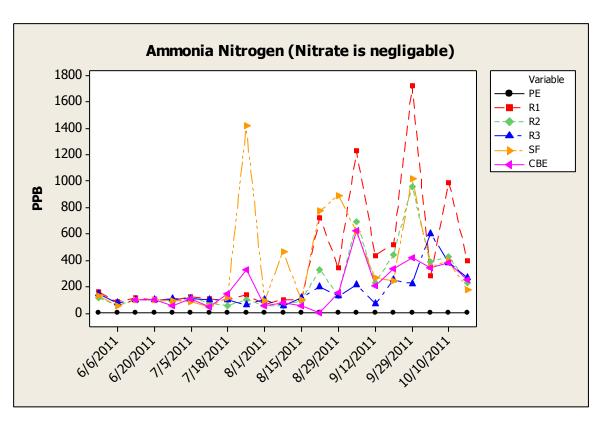


Figure 11. Time Series Plot of Nitrogen as Ammonia.

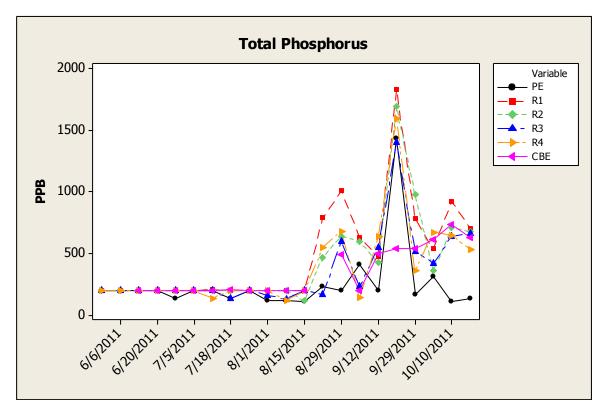


Figure 12. Time Series Plot of Total Phosphorus.

No attempt was made to increase the temperature of water input to the system since the temperature of pond effluent samples was stabilized near the average of 10.5 °C throughout the entire operating period as shown in **Figure 13**. These water temperatures are significantly higher than those observed during a brief operation in September through November 2010 at the South Rasmussen mine, where little Se removal was primarily attributed to cold weather coupled with the lack of an established Se reducing population. Beginning in early July, the temperature of bioreactor and sand filter effluent was 50% higher than the pond effluent. This increase in water temperature through the system is indicative of potentially an expenditure of excess energy from microbial activity, and it is observed that the onset of this marked temperature increase corresponds with reactor and pond effluent Se levels above 5 ppb.

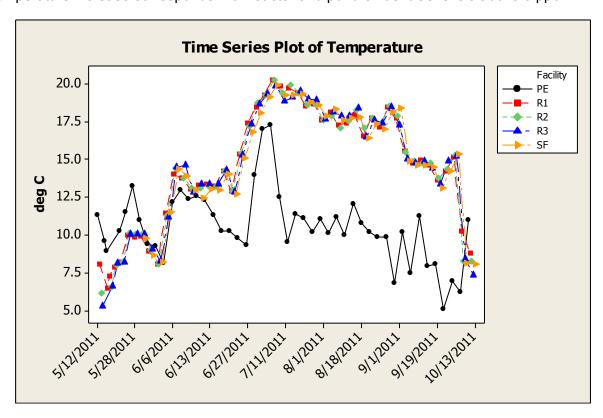


Figure 13. Time Series Plot of Influent and Effluent Temperature.

TOC concentration in bioreactor and sand filter effluents were higher than pond effluent as shown in **Figure 14**, indicating excess carbon nutrient was used to drive microbial respiration of dissolved selenium. Irregardless of the excess carbon fed to the system, there were no instances of severe pluggage due to the accumulation of biomass or other particulate matter similar to that experienced during the 2008 pilot study. Lower carbon substrate addition was intentionally used to prevent these operational issues that typically require fluidization and/or backwashing operations. Figure During periods when the system effluent was being recirculated to the pond, the residual TOC in the system effluent was likely causing Se removal within the pond due to the presence of selenium-reducing bacteria in the pond coupled with the long residence time.

The target carbon nutrient concentration input to the process was set at 10 ppm TOC to mitigate potential fouling and pluggage issues from excessive microbial growth. However, the residual TOC measured in system effluent samples was consistently above 10 ppm. This showed more carbon was being fed to the system than was being consumed. During these studies biological oxygen demand (BOD) was also measured (data not shown). In the future it is proposed to eliminate BOD from the analyte list. In complex waste water streams there is some advantage to measuring both TOC and BOD as not all organic carbon is readily available for biodegradation. However, in a relatively clean system that is being dosed with a labile carbon source, TOC and BOD are essentially equivalent. The measurement of BOD is cumbersome, is plagued by many complicating factors, and is poorly reproducible. In contrast, TOC measurement is straight forward and highly reproducible, and thus measurement of only TOC in the future will provide the data required for bioreactor operation and optimization.

The carbon nutrient source was changed from MicrocG® to a mixture of methanol and molasses on July 26th, and shortly thereafter TOC levels in bioreactor and pond effluent dropped significantly due to decreased carbon nutrient flow as shown in **Figure 15**. The new carbon nutrient source, methanol and molasses, was diluted with pond water to reduce the flash point because the mixture is stored in a 250 gallon tank in an enclosure where fumes could buildup if it was not diluted. (See **Figure 3**). The carbon nutrient source is added to the pond effluent (raw water feed) through an eductor installed on a small bypass stream that is recombined to the common raw water feed immediately upstream from the bioreactor influent header. Due to issues maintaining control over accurate and consistent carbon addition and potential air infiltration through the eductor, improved carbon addition equipment should be considered for future operation.

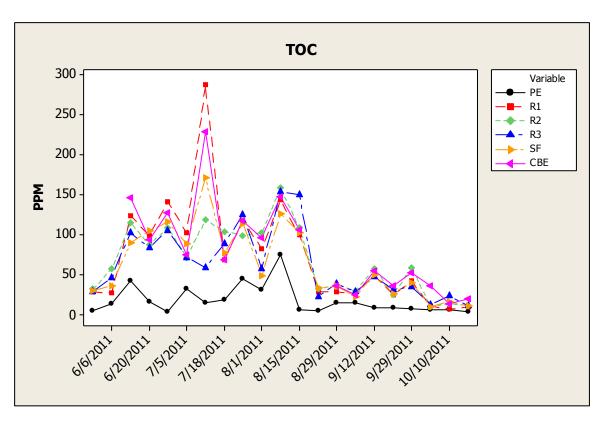


Figure 14. Time Series Plot of TOC.

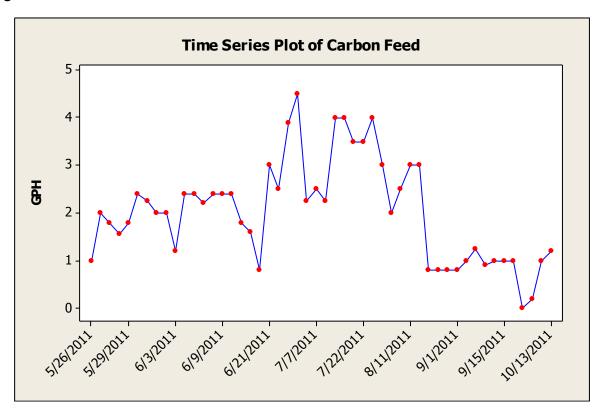


Figure 15. Time Series Plot of Carbon Nutrient Flow Rate.

After dosing with carbon nutrient, pond effluent is distributed to a common header which is then split between the three bioreactors. The flow rate for the total system and each bioreactor train influent is depicted in Figure 16. The total system can be supplied from one pump (~13 gpm) or two pumps (~26 gpm). Between June 3rd and July 11th the total system flow was supplied at the lowest flow rate for the longest period of time. This time period corresponds with the lowest dissolved Se effluent levels in Figure 7, and indicates that the lower flow and resulting longer residence time are key variables in approaching the Se effluent target. It is notable that carbon nutrient flow rates do not correlate with total system flow in Figure 16. This indicates that periods of low flow were accompanied by relatively high carbon nutrient addition, and the decreased Se level in the system effluent experienced in early July was due to a combination of low flow and elevated carbon nutrient addition. It is recommended that the lower flow one-pump operation be set as a critical limit not to be exceeded during future operations. Rather than recirculating to the retention pond to maintain sufficient water level for consistent feed, the system should be set at the lowest flow possible and if pond levels fall below the level needed to maintain system flow then the bioreactors should be filled for a static growth period with an excess supply of nutrient until the pond refills to feed the system at the lowest feed rate attainable.

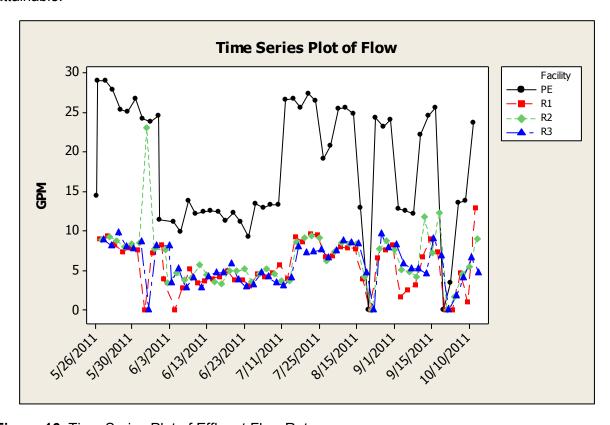


Figure 16. Time Series Plot of Effluent Flow Rate.

One criteria for the success of this system is the ability to control multiple metals in addition to Se, including As, Cd, Ni, and Zn. Many of the control technologies available for Se remediation are not able to control other metals due to chemical differences inherent to various species. For example, As and Se are present as oxyanions whereas Cd, Zn, and Ni are polycationic. The

anaerobic bioreactor system offers two mechanisms to remove metals, including direct enzymatic reduction to insoluble elemental forms, and reduction of sulfate to form sulfide anions to precipitate cationic metal ions as insoluble metal-sulfide species. This system demonstrated the ability to reduce levels of these metals in bioreactor effluent samples throughout operations presumably utilizing both mechanisms.

Although the total As level in the retention pond is below IDSWQS for dissolved As (150 ppb), the bioreactors consistently reduced As below 5 ppb. **Figure 17** provides an example of total and dissolved As in reactor 3 effluent, which is representative of the other trains and the sand filter. The difference between total and dissolved As levels is not as significant as the difference between total and dissolved Se observed in **Figure 6.** This suggests that either As particulate are larger than Se particulate and are more able to be captured by the system, or As particulate are below 45 µm and cannot be filtered prior to analytical characterization.

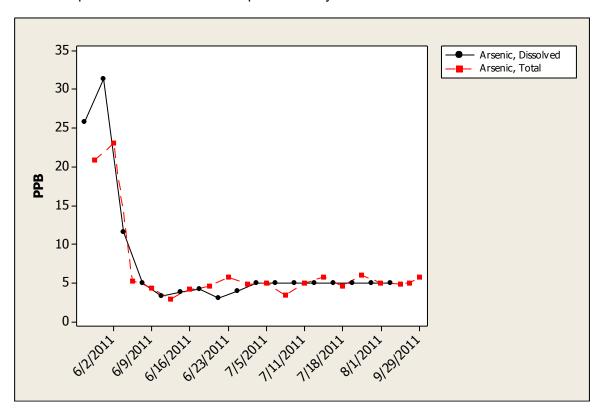


Figure 17. Time Series Plot of Total (red) and Dissolved (black) Arsenic in Reactor 3 Effluent.

The IDSWQS for dissolved Cd is considerably lower than other metals at 1.3 ppb (See Table 1 with footnotes) and has been calculated based on hardness. Cd concentrations in the retention pond varied above this level between 2 and 14 ppb, and the bioreactor system was able to reduce dissolved Cd below the analytical method detection limit (MDL) of 1.5 ppb) as shown in **Figure 18**. Every attempt will be made for future Cd analyses to ensure that the MDL is below the IDSWQS to confirm that the level of Cd removal is consistent with IDSWQS. However, it should be noted that because of the high concentration of calcium and magnesium in the samples, this may not be possible. The MDL established by the laboratory is 0.3 ppb but because of interferences due to the high concentrations of calcium and magnesium in the

sample, all sample had to be diluted fivefold, thus raising the MDL above the IDSWQS for cadmium.

As shown in **Figure 19** and **Figure 20**, zinc levels were consistently between 1 and 2 ppm in the Pond. As water treatment progressed, the Zn levels in bioreactor and sand filter effluent dropped below the MDL of 62.5 ppb..

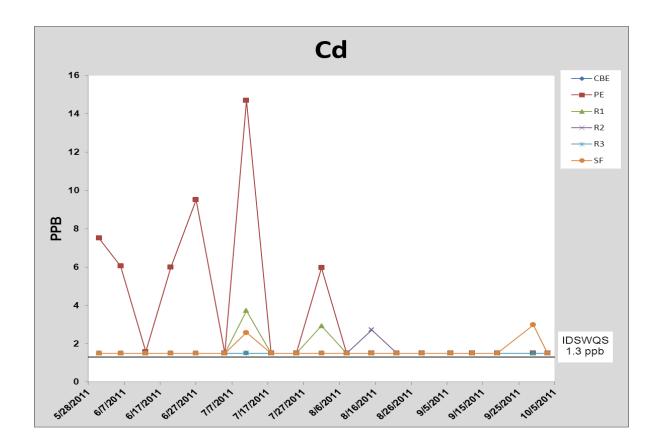


Figure 18. Time Series Plot of Dissolved Cadmium in Influent and Effluent Samples.

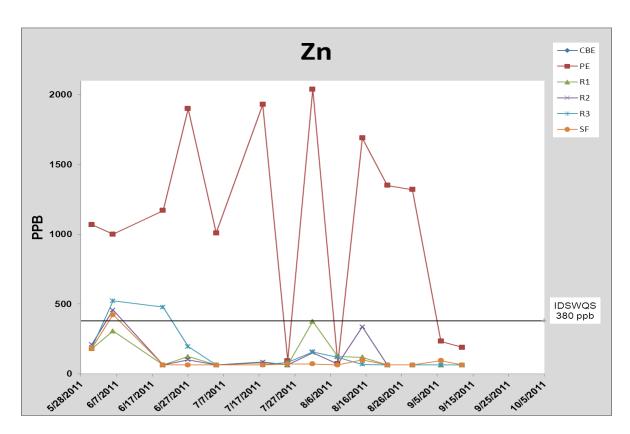


Figure 19. Time Series Plot of Dissolved Zinc in Influent and Effluent Samples.

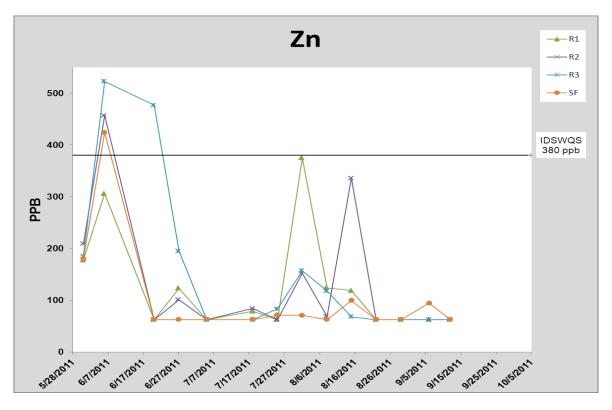


Figure 20. Time Series Plot of Dissolved Zinc in Bioreactor and Sand Filter Effluent Samples.

The mechanism for removal of Cd and Zn is presumably sulfide precipitation since sulfate has a lower redox potential than Cd and Zn. The levels of sulfate shown in **Figure 21** are considerably higher than those of Cd and Zn at ~1500 ppm, and the sulfate levels were slightly lower after July due to the decreased system ORP. This lower sulfate level is indicative of the formation of sulfide, some of which evolves as $H_2S(g)$ and contributes to the localized odor and the ability to precipitate cationic metal ions. For example, Ni was removed below the IDSWQS (170 ppb-See Table 1 with footnotes) around the same time that sulfate levels began to drop in the mid July timeframe. This decrease is shown in **Figure 22**, where the highest pond Ni concentration of 947 ppb was reduced to 46 ppb on July 11th, and was maintained below the 170 ppb limit for the remainder of the operating season. Eight weeks were required to achieve Ni removal to this level. This is attributed to the lag time required to get to sulfate-reducing conditions to allow the precipitation of Nickel sulfide. It is probable that consistent Ni removal below 170 ppb could be achieved by decreasing the system flow rate.

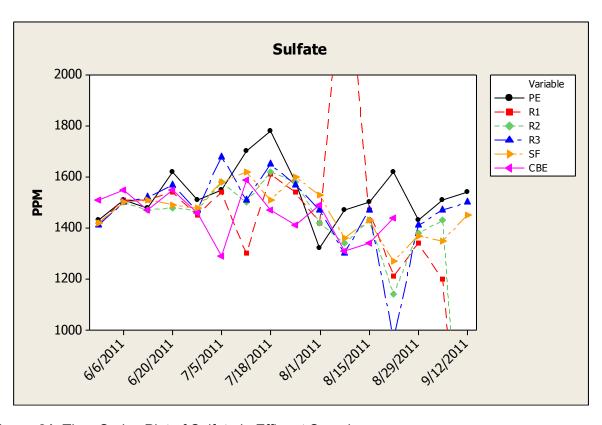


Figure 21. Time Series Plot of Sulfate in Effluent Samples.

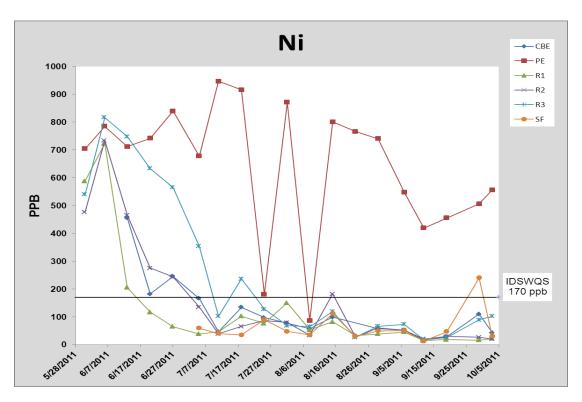


Figure 22. Time Series Plot of Nickel in Effluent Samples.

Conclusions and Recommendations from Pilot Test

In summary, the three train bioreactor system treated a combined volume of over 3 million gallons over the course of the pilot study. Although selenium was not consistently removed below 5 ppb, the system removed approximately 12.5 pounds of a total of 16 pounds of Se that passed through the system for a 70% efficiency for removal of total Se. For the majority of the operating season, total and dissolved Se concentrations were between 99% and 80%. Neither of the three trains demonstrated greater Se removal or consistency which suggests negligible impacts from the growth media composed of limestone and activated carbon. The system also demonstrated good ability to control Cd, Zn, As, and Ni, and total metals control could be improved by utilizing a lower system flow rate.

In order to utilize the learnings from the bioreactor trends discussed herein to optimize bioreactor performance to consistently meet Idaho surface water quality standards, a number of recommendations are made for consideration prior to startup next season.

- 1. Test the minimum total system flow to allow longer residence time to effectively reach 5 ppb total Se , or run two of the trains in sequence to increase hydraulic residence time.
- Do not re-circulate system effluent to the pond to mitigate the influence of treated water on the pond water chemistry. This could be difficult as the some pond water needs to me maintained to run the system.

- Install an alternative carbon dosing system that will allow consistent and accurate dosing without introducing additional air infiltration. Peristaltic and piston based pump systems should be investigated further improve sand filtration to increase removal of particulate Se.
- 4. Cap the secondary influent distribution system for each train to force the influent to pass through the reactive media. Ensure that the access ports on the top of each train are in place to mitigate the infiltration of leakage oxygen.
- 5. Continue to use methanol/molasses mixture as a reparable carbon substrate rather than more costly MicrocG®.
- 6. Possibly conduct a tracer study utilizing Li or Br species to identify the flow paths and retention times for each train.
- 7. Consider utilizing alternative carbon microbial growth mediums.
- 8. Eliminate the analytes that weren't present in the dump seep during the 2011 campaign. and focus on key analytes, including: total and dissolved Se, dissolved Ni, Cd, Zn, TOC, DO, ORP, pH, Temperature,
- 9. Conduct laboratory support studies to identify operating trends and flexibilities to consistently meet target Se concentrations

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